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Method for the Continuous Production of Liquid Resols

Abstract

The invention relates to a method for the continuous production of liquid resols that are used as bonding agents for the production of particle and fiber boards, mineral and textile-fiber mats, foundry cores and shell molds, abrasive tools, and grinding belts. The objective of the invention is a method for the continuous production of a wide palette of differently applicable products, whereas the method can easily be adapted to the different products. The task of the invention is the application of a continuous multi-step process that keeps the molar-mass distribution within narrow limits and avoids gel formation, also with highly concentrated products.

According to the invention, the poly-condensation takes place in a multi-chamber reactor in which the formalin used is converted step-wise up to at least 80%, without forced circulation and at normal pressure, while being simultaneously concentrated by distillation--or in one step, without concentration by distillation.

Patent claims

1. Method for the continuous production of liquid resols by polycondensation of phenols with formaldehyde, in a molar ratio of 1:1 in the presence of a basic catalyst, characterized in that the polycondensation takes place, without forced circulation and at normal pressure, in a multi-chamber reactor consisting of several heatable reaction chambers located above each other, whereby

   a. the formaldehyde used is first converted up to at least 50% and the further conversion up to at least 80% takes place with simultaneous concentration by distillation, up to a solids content of maximally 90; or

   b. the conversion of the formaldehyde used takes place up to at least 80, without concentration by distillation.

2. Method according to claim 1, characterized in that a part of the raw materials is continuously supplied to one or several reaction chambers below the upper reaction chambers.

Description

The invention relates to a method for the continuous production of liquid resols by polycondensation of phenols with formaldehyde in the presence of basic catalysts. The resols produced according to this method can be used in different branches of the national economy. For instance, they are used as bonding agents for the production of particle and fiber boards, mineral and textile-fiber mats, foundry cores and shell molds, abrasive tools, and grinding belts.

The technical production of resols by poly- condensation of phenols with formaldehyde, at molar ratios of 1:>1 in the presence of basic catalysts takes place almost exclusively in a batch operation in heated agitator reactors--if necessary, with subsequent concentration of the formed polycondensate by distillation under a vacuum.

The continuous methods, familiar until now, for the production of liquid resols are mostly suitable only for a very narrow assortment of special types or possess different drawbacks that restrict their technical usability.

The apparatuses used for the continuous production of liquid resols contain, for the most part, several in part different aggregates whose adjustment to each other requires high expenditures for measurement and technical control and that are connected with high investment costs as well as high operating and energy costs for the production of vacuum or pressure, the drive of agitators, cleaning, and maintenance.

Methods that allow only the production of a very restricted assortment of special resols are described in US-PS 26 88 606, DD-AP 82 834, and US-PS 36 57 188. Methods with high investment and operating costs are represented in US-PS 26 58 054, DE-AS 15 95 035, and DE-AS 17 20 306.

A relatively variable method that uses simple apparatuses is described in DD-WP 134 354. The drawbacks in these methods are the pumps required for the production of a circulation of the reaction mixture and that are impacted with the hot reaction mixture whereby sealing problems arise; the necessary accurate control of the valves between the reaction steps; and the vacuum in the second reaction step required for the concentration of highly condensed resols, to avoid gel formation.

In addition, because of the low number of reaction steps, an increased stress on the waste water with non-converted raw materials and a very wide molar mass distribution in the resols has to be reckoned with.

According to DD-WP 311 and DE-AS 23 64 088, the continuous

production of phenol resins is carried out in a horizontal reactor subdivided by partitions into several chambers. Both methods have the drawback that--with those kinds of resols that, during the polycondensation or the treatment by distillation, suffer a phase separation into a resin-like and an aqueous phase --a continuous passage of the reaction mixture from chamber to chamber cannot be guaranteed.

The goal of the invention is a method for the continuous production of liquid resols that avoids the drawbacks of the familiar technical solutions. In particular, a method is to be developed that allows the production of a broad palette of differently usable products, has a simple structure and can be operated with low operating and energy costs.

It is the task of the invention to carry out the polycondensation and the optionally required concentration of the formed polycondensate in such a multiple-step process that an unjustifiable expansion of the molar-mass distribution and the danger of gel formation are avoided, also in highly concentrated products. Another task of the invention is to guarantee--without the use of aggregates, e.g., agitators or pumps, that make possible the use of a forced circulation--an unimpeded passage of the reaction mixture through all steps of the process, also with those kinds of resols that suffer a temporary phase separation into a resin-like and an aqueous phase during their production.

Another task of the invention consists in designing the method in such a manner that it can be implemented in all steps of the process without the use of a vacuum or increased pressure.

The method according to the invention is carried out in a multi-chamber reactor consisting of an arbitrary number, adapted to the products to be produced, of heatable reaction chambers placed one above the other. Each reaction chamber is equipped with an overflow pipe that, advisedly, runs through the bottom of the reaction chamber into the reaction chamber below and extends into the latter so that it dips into the reaction mixture present in this reaction chamber.

In addition, each reaction chamber has a connecting piece for the discharge of steam, attached above the overflow pipe, that advisedly leads laterally to the outside.

According to the invention, the reaction mixture consisting of phenol, formaldehyde in the form of its aqueous solution, and a basic catalyst in the weight ratio specified by the recipe is simultaneously continuously introduced into the upper reaction chamber of the multi-chamber reactor and flows from there, through the overflow pipes available in each reaction chamber, successively through the individual reaction chambers from top to bottom.

If necessary, the reaction mixture can be preheated in a heat exchanger connected in series ahead of the multi-chamber reactor.

By phenol is to be understood, in the sense of the invention, the phenol itself as well as its homologs and derivatives, or mixtures of the same.

In the reaction chambers, which are under normal air pressure, the reaction mixture is constantly kept at the boiling point--by the exothermal polycondensation reaction and, if required, by additional heating--at a temperature of 373K, with the result that, in each reaction chamber, a sufficient turbulence of the reaction mixture is produced by the rising steam bubbles.

If, during the polycondensation, no phase separation of the reaction mixture sets in, the reaction mixture can be brought to reaction in all or in part of the reaction chambers at a temperature that lies under the boiling temperature of 373K.

During the production of liquid resols that are not in need of a concentration by distillation, the steam formed during the boiling is supplied to a heat exchanger through the steam pipe by way of a common steam supply line, condensed in the heat exchanger, and returned as steam condensate into the upper reaction chamber of the multi-chamber reactor. In this manner, the polycondensation takes place with reflux of the steam condensate.

The adjustment of the average retention time of the reaction mixture in the multi-chamber reactor takes place by constant metering of the reaction mixture in tune with the effective volume of the multi-chamber reactor. The retention time is to be adjusted in such a manner that, in the multi-chamber reactor, at least 80% of the used formaldehyde is converted. The finished liquid resol exiting from the bottom reaction chamber of the multi-chamber reactor by way of the overflow tube is cooled in a heat exchanger connected subsequently in series and is supplied to a storage tank.

If liquid resols are to be produced that need concentration by distillation, a modified mode of operation is necessary. In this case, only the steam rising from the reaction chambers located in the upper part of the multi-chamber reactor is returned to the upper reaction chamber, after condensation in the heat exchanger, while the steam rising from the reaction chambers located in the lower part of the multi-chamber reactor is discharged as waste water, after condensation in a second heat exchanger.

In any case, the reaction chambers located in the bottom part of the multi-chamber reactor are to be heated in such a manner that they receive the evaporation heat necessary for concentration by distillation.

Depending, in each case, on the degree of the concentration attained in the individual reaction chambers in the bottom part of the multi-chamber reactor, the temperature in the reaction chambers from above to below rises from 373K to maximally 388K.

By the metering of the reaction mixture and an efficient division of the multi-chamber reactor into the upper part operating with reflux of the steam condensate and the lower part operating with discharge of the steam condensate, and the effective volumina in these parts of the multi-chamber reactor, the average retention times of the reaction mixture in the parts of the multi-chamber reactors are adjusted in such a manner that, in the upper part of the multi-chamber reactor, at least a 50% conversion of the metered formaldehyde--and, in the lower part of the multi-chamber reactor, at least an 80 conversion of the metered formaldehyde--is attained.

The concentration of the liquid resols can take place up to a solids content of 90% whereas, however, the viscosity of the liquid resols at the temperature prevailing in the last reaction chamber cannot exceed 50 mPa·s.

The finished liquid resol exiting from the bottom reaction chamber of the multi-chamber reactor by way of the overflow pipe is cooled in a heat exchanger connected subsequently in series and is supplied to a storage tank.

Other modifications of the methods are possible by metered addition of a part of the raw materials--not into the upper reaction chamber, but into one or several of the other reaction chambers of the multi-chamber reactor.

Examples of Operation

Example 1

Continuous production of a liquid resol without concentration by distillation

180 kg of a technical cresol mixture with a content of 32-34% of m-cresol, 240 kg of a 30% formalin, and 80 kg of a 40% caustic soda solution are metered, per hour, in an even flow, into the upper reaction chamber of a multi-chamber reactor, with an effective volume of 0.6 m^3, consisting of 4 heated reaction chambers placed on top of one another.

By the exothermal reaction and by additional heating, a temperature of 100°C is maintained in all reaction chambers. The steam rising from the reaction chambers is condensed in a heat exchanger, and the condensate is returned into the upper reaction chamber of the multi-chamber reactor. The average retention time of the reaction mixture in the multi-chamber reactor is 80 minutes under the specified conditions.

The finished liquid resol flows out of the multi-chamber reactor by way of the overflow pipe of the last reaction chamber, in an amount of 500 kg per hour. It is cooled in a heat exchanger, connected subsequently in series, to a temperature of 40°C, and supplied to a storage tank.

The product has the following characteristic values:

Solids content	43-45%
Viscosity at 20°C	500 ± 100 m Pa·s
Content of free formaldehyde	1,5 ± 0.5%

and serves as a bonding agent for the production of particle boards.

Example 2

Continuous production of a liquid resol by means of concentration by distillation

For the production of this resol, a multi-chamber reactor consisting of eight heatable reaction chambers placed on top of one another is used. The upper five reaction chambers with an effective volume of 0.75 m^3 are connected in such a manner that the steam rising from them during the operation is condensed in a heat exchanger and is supplied as a condensate into the upper reaction chamber of the multi-chamber reactor, while the lower three reaction chambers, with an effective volume of 0.45 m^3, are connected in such a manner that the steam rising from them is condensed in a second heat exchanger and discharged as waste water.

250 kg of an 80% aqueous phenol solution, 200 kg of a 30% formalin, and 5.0 kg of a 45% caustic soda solution are metered, per hour, in an even flow, into the upper reaction chambers of the multi-chamber reactor. By the exothermal reaction and by additional heating, the metered reaction mixture is constantly kept boiling at 100°C in the upper five reaction chambers, and the rising steam is returned to the upper reaction chamber after condensation.

The average retention time of the reaction mixture in the upper five reaction chambers is 105 minutes under the specified conditions. The reaction mixture discharged from the overflow of the fifth reaction chamber into the sixth reaction chamber contains 4.8% of free formaldehyde, which corresponds to a conversion of 70%.

The bottom three reaction chambers are heated in such a manner that 135 kg of waste water is distilled from them per hour. The reaction mixture in the last reaction chamber is heated to a temperature of 105-106°C.

The average retention time of the reaction mixture in the bottom three reaction chambers is 75 minutes under the specified conditions.

The finished liquid resol flows out of the overflow pipe of the last reaction chamber in a quantity of 320 kg per hour. It is cooled, in a heat exchanger connected subsequently in series, to 55°C and supplied to a storage tank. The product contains maximally 1.5% of free formaldehyde, which corresponds to a conversion of at least 90%.

The product has the following characteristic values:

Solids content	74 ± 1%
Viscosity at 20°C	3000 ± 200 mPa·s
B time at 100°C	200 ± 30 s

and serves as a bonding agent in the production of abrasive tools.

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